

VOCs and Regional Ozone: Field, Lab and Model Results

Peter G. Green

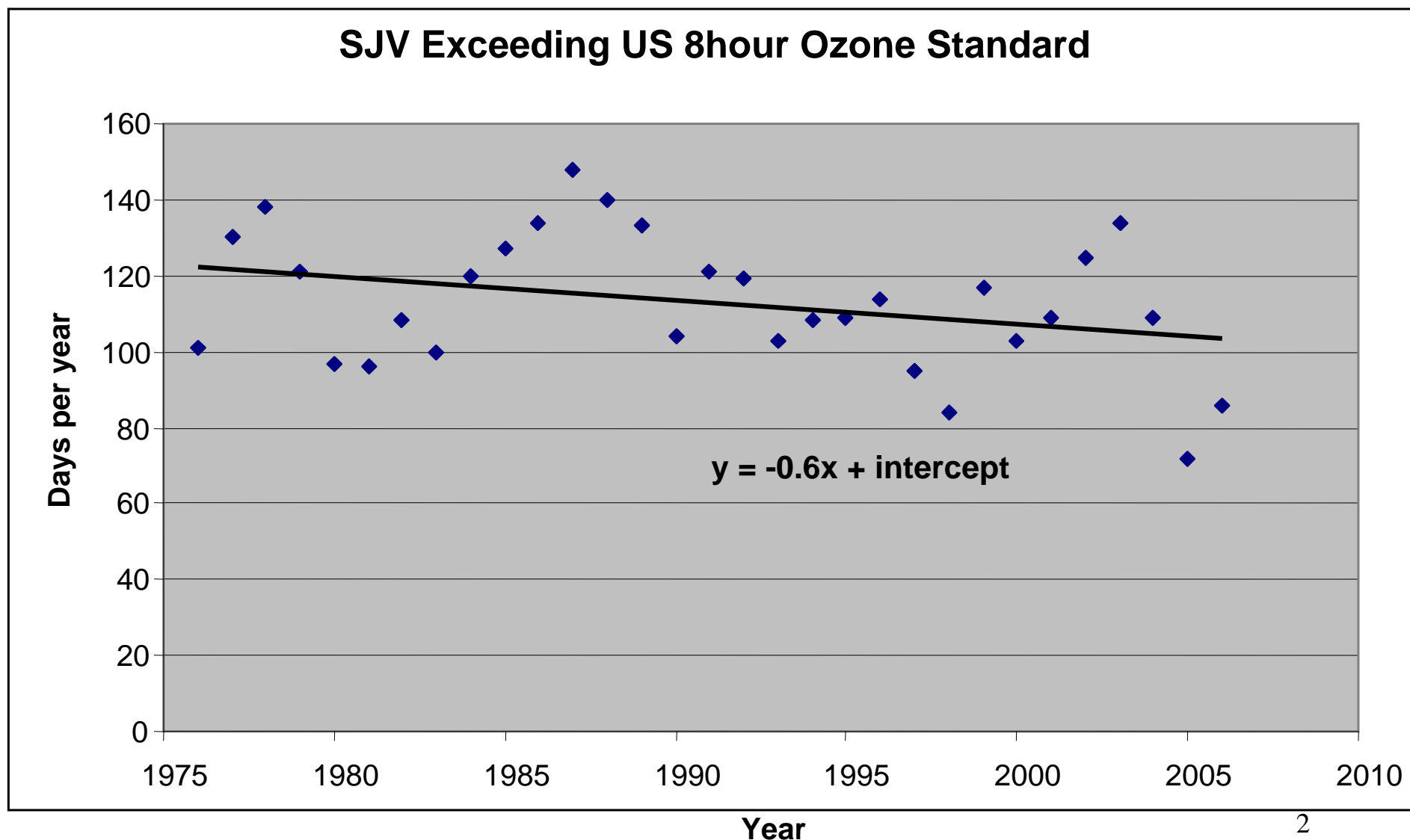
Dept of Civil & Environmental Engineering
PGGreen @ UCDavis.edu

Funds: USDA Special Projects, through CSREES
(Cooperative State Research Education and Extension Service)

Profs. Bob Flocchini and Mike Kleeman,
Drs. Wenli Yang and Anuj Kumar,
Cody Howard and Doniche Derrick,
Dr. Frank Mitloehner and his group,
plus an anonymous company.

San Joaquin Valley ozone improving, but too slowly

(2005 was best yet, but also note ~1980, ~1998 and 2003)



Ozone Cycle and the Dependence on NO_x and VOC:

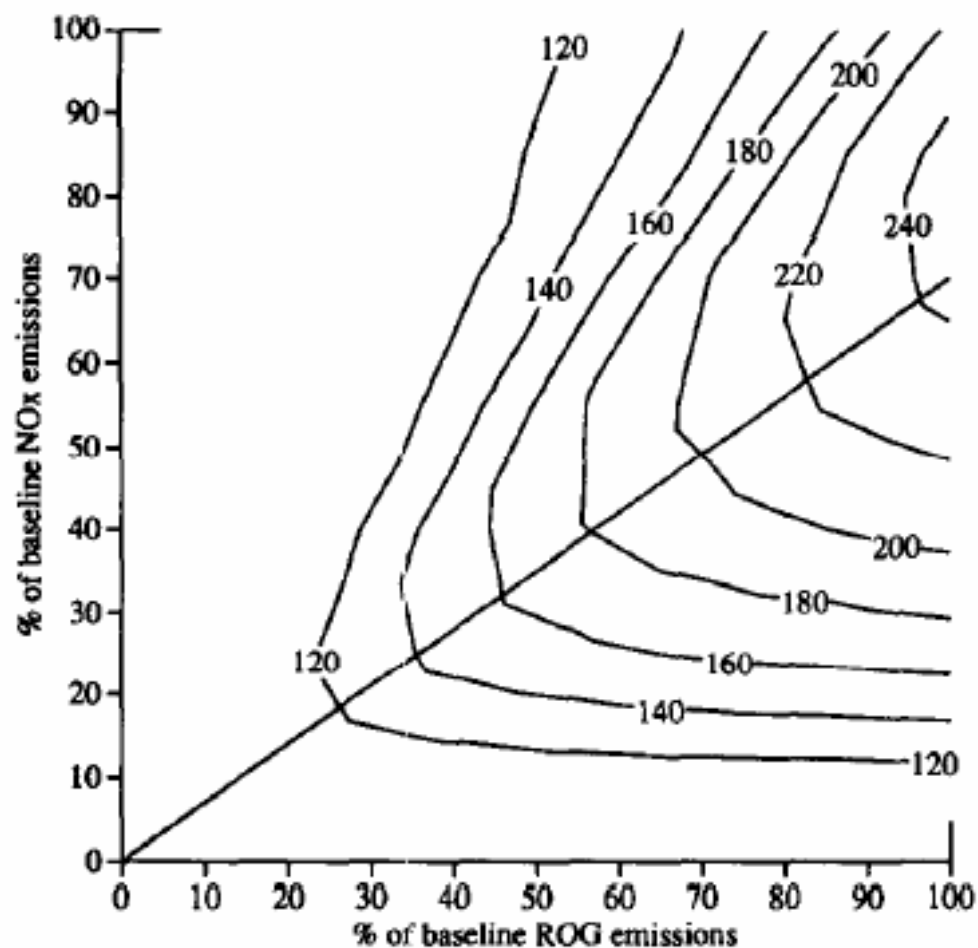
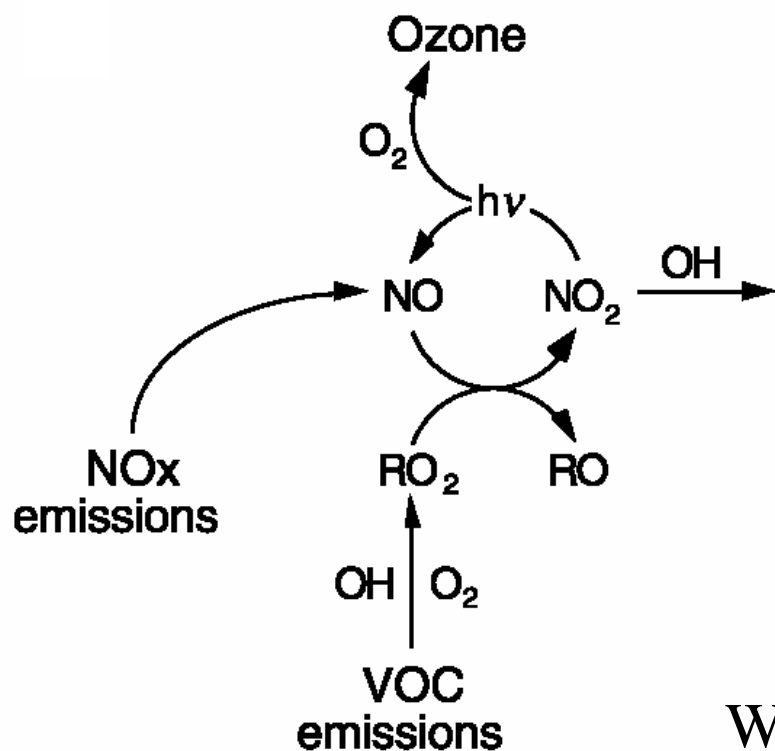
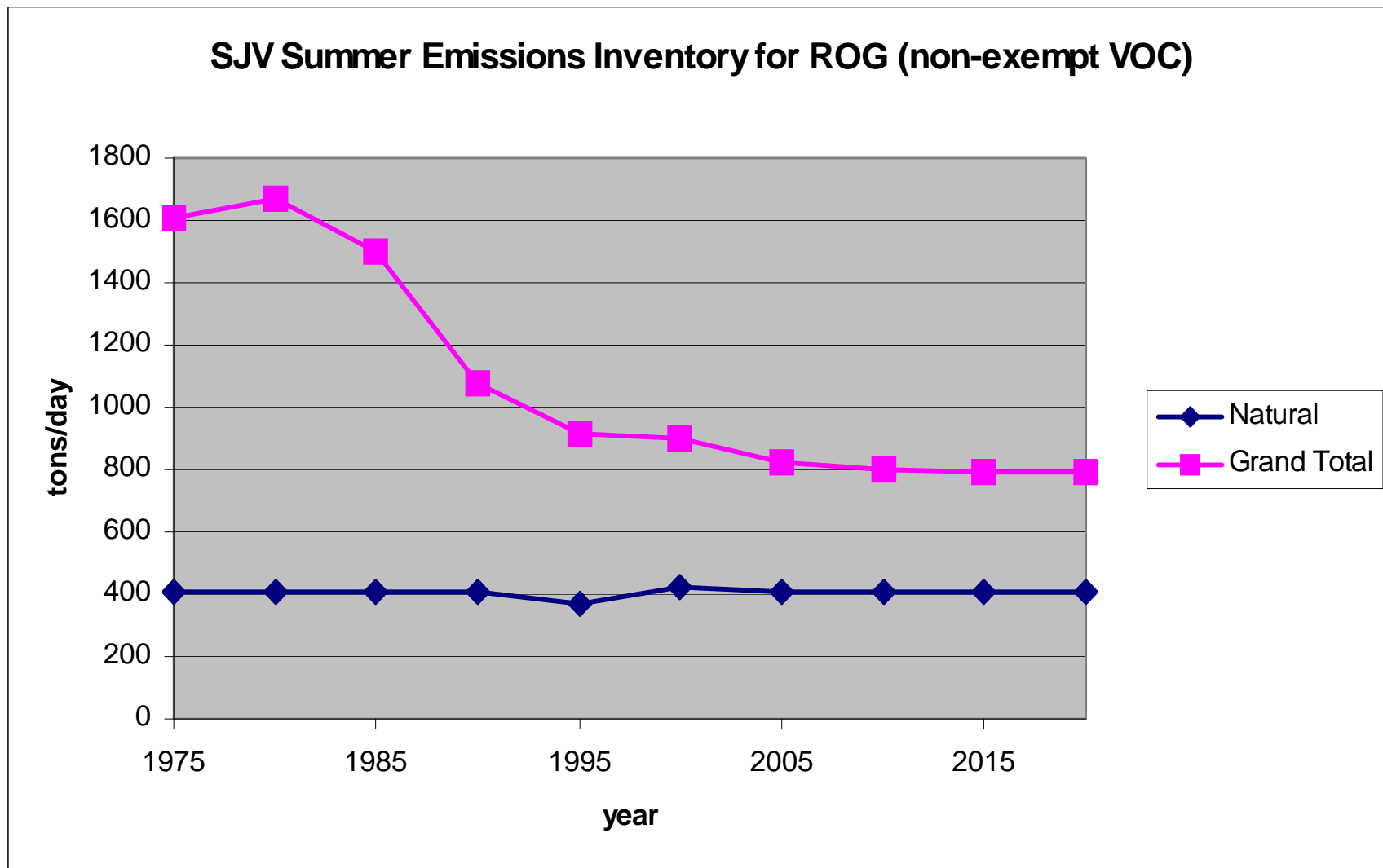
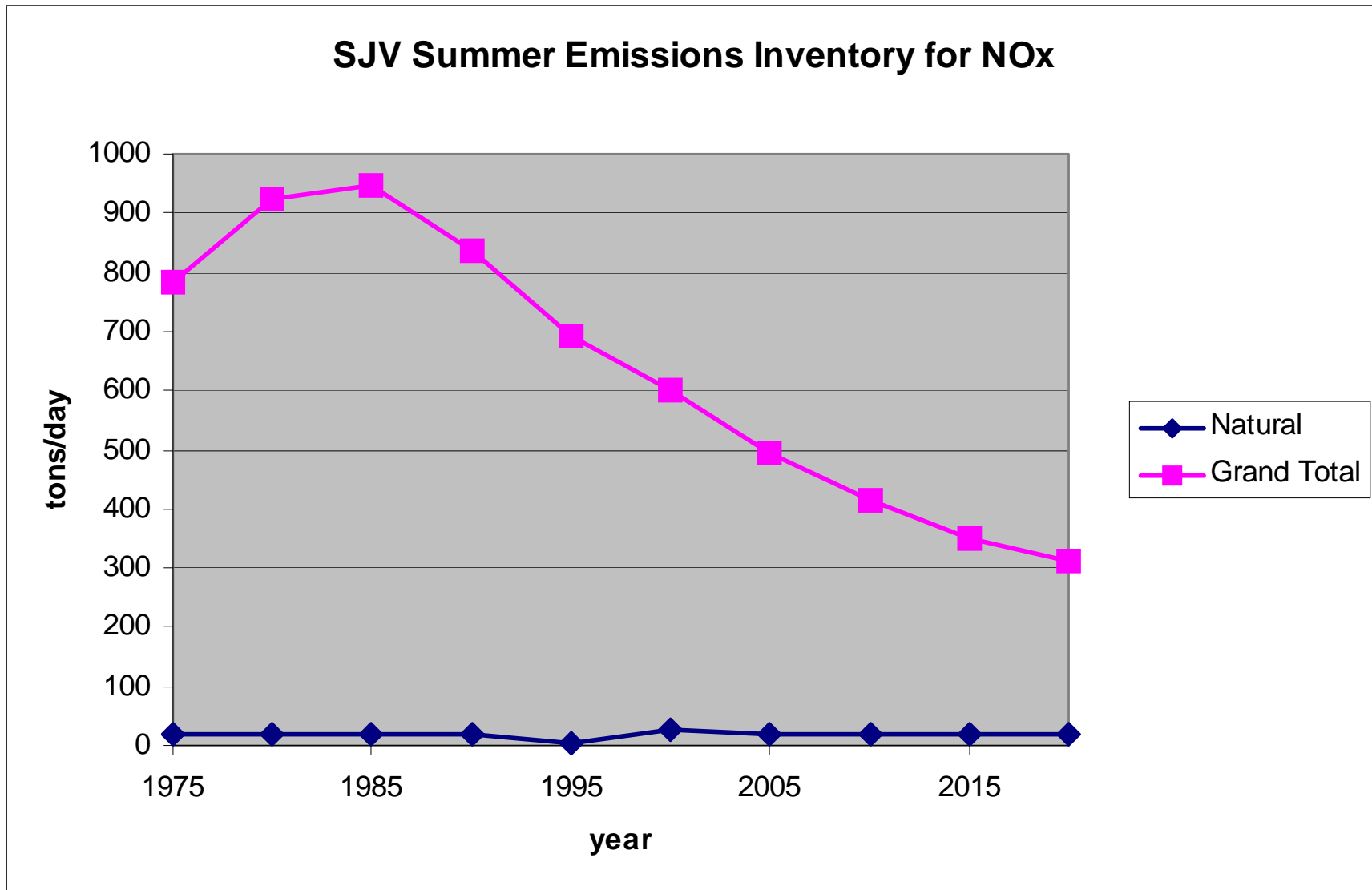


Fig. 1. Ozone isopleth diagram showing the hypothetical response of peak 1 h average ozone concentrations within an air basin to changed levels of anthropogenic ROG and NO_x emissions. Contour lines are lines of constant ozone concentration (ppb).

Total Reactive Organic Gases (non-exempt VOCs) have actually been quite greatly reduced.



NOx show a delayed trend/forecast
-- and monitoring data suggests may be slower



Since $\text{VOC} + \text{NO}_x + \text{light} \Rightarrow \text{Ozone}$
then why isn't SJV Ozone improving?

- Idea#1: Reactive organic gases are still available in excess to the limiting reagent (NO_x)
 - and natural background limits our ability to lower VOCs
- Idea#2: Until NO_x emissions are also sufficiently reduced, ozone may not improve, or not improve enough
- Idea#3: May also need more improvements upwind
- Fact: Different compounds do not react equally
 - So, reducing total pounds may not reduce reactivity
 - And therefore not reduce ozone

2007 SJV Implementation Plan gives precedence to NO_x reductions, and mentions:

- Ingenuity
- No stone unturned
- Incentive-based measures
- Technology advancement
- Most cost-effective way
- Innovative

VOC reductions will also help,
especially for more reactive compounds

Great variation in formation potential (lbs. ozone per lb. VOC) even among similarly volatile molecules

Molecule	Boiling Point, C	MIR
acetic acid	118	0.5
butyl acetate (n-)	118	0.89
octane	126	1.11
butanol (n-)	125	3.34
octene (1-)	121	3.45
toluene	111	3.97
xylene (para,ortho,meta)	139	4.2,7.5,10.6

Also considerable variation within a family of VOCs, e.g. alcohols, etc...

From a regulator: Unfortunately, this may be one issue where the legal system hinders [progress]. We are legally required ... the inventory is calculated based on mass not reactivity.



- Regulations already do consider VOC reactivity
 - By either exempting, or counting by total mass
- We must further consider the relative reactivity,
-- to best improve air
- Typical past studies for urban air use high NO_x
 - We use levels typical for summer in San Joaquin Valley
- More diverse types of molecules in rural VOC
 - Some unstable, others mutually incompatible
 - We assess the entire sample of air at the source, and assess ozone formation from the entire sample

CANISTER COMPARISON STUDY RESULTS

Table 2. Compound Percent Difference From Assigned Value

COMPOUND	PERCENT DIFFERENCE	COMPOUND	PERCENT DIFFERENCE
Ethane	0	Methylcyclopentane	-1.6
Ethene	-5.3	2,4-Dimethylpentane	-3.1
Propane	-2.5	Benzene	-11
Propene	-9.7	Cyclohexane	-3.5
Isobutane	-5.3	2-Methylhexane	1.3
Butane	-2.2	2,3-Dimethylpentane	15.8
Ethyne	-49.7	3-Methylhexane	1.9
t-2-Butene	-2.8	2,2,4-Trimethylpentane	0
1-Butene	-7.2	Heptane	-1.9
c-2-Butene	-7.8	Methylcyclohexane	-3.1
3-Methylbutene	-8.4	2,3,4-Trimethylpentane	-0.6
2-Methylbutane	-1.3	Toluene	-7.8
1-Pentene	-6.3	2-Methylheptane	-1.3
Pentane	-1.6	3-Methylheptane	0
Isoprene	-16	Octane	-1.3
t-2-Pentene	-4.3	Ethylbenzene	-14.4
c-2-Pentene	-5	m/p-Xylene	-20.1
2-Methyl-2-Butene	-18.8	Styrene	-57.2
2,3-Dimethylbutane	-2.2	o-Xylene	-13.8
Cyclopentene	-9.1	Nonane	-8.5
4-Methylpentene/	-3.5	Iso-Propylbenzene	-17.3
3-Methylpentene	-5.9	alpha-Pinene	-32.4
Cyclopentane	-2.2	n-Propylbenzene	-55.2
2,3-Dimethylbutane	1.6	1,3,5-Trimethylbenzene	-18.4
2-Methylpentane	0	1,2,4-Trimethylbenzene	-20.1
3-Methylpentane	-88.7	Decane	-23.9
2-Methylpentene	-0.3	beta-Pinene	-70.1
Hexane	-5.3	t&c-2-Hexene	-2.2

ARB has a
Photochemical
Assessment
Monitoring
Station
(PAMS)
network
-- but cannot
measure dairy
VOCs from a
cannister

Complexity of rural ozone formation

- Diverse mixture of VOCs
- Even with multiple techniques, no ‘total’
- Substantial natural background
- Proprietary VOCs
 - Cannot purchase and/or apply freely to study
- Induced emissions (soil, plant)
- Non-registered usage
- NO_x limitation
- Upwind sources

Since we can't bring whole
rural air into the lab,
we're taking the lab out to the air.

Since total VOCs cannot be measured,
we measure the ozone they would make.

Measure VOCs with multiple techniques

Assess upwind ozone formation

Mobile Ozone Chamber Assay (MOChA)



Graduate students Cody Howard and Doniche Derrick.

Field Operations

- Flush with zero air between experiments
- Teflon diaphragm pump quickly loads 1000L of air
- Monitors for NO+NO₂ (=NO_x), Ozone
- Also temperature, humidity, UV intensity in chamber
- Meteorology (wind, etc...) for dispersion modelling
- Produce photo-chemical ozone in ~2-3 hours
- INNOVA for real-time measurement of up to 6 gases
- Cannisters, sorption tubes, derivatization for varied VOCs
- Roughly 4 hour cycle time – start 8am, 12noon, 4pm
- Mobile – can move with pick-up truck
 - And is on wheels!

Mobile Ozone Chamber Assay (MOChA)



Separate lamp unit, with fans to aid temperature control.

MOChA 2

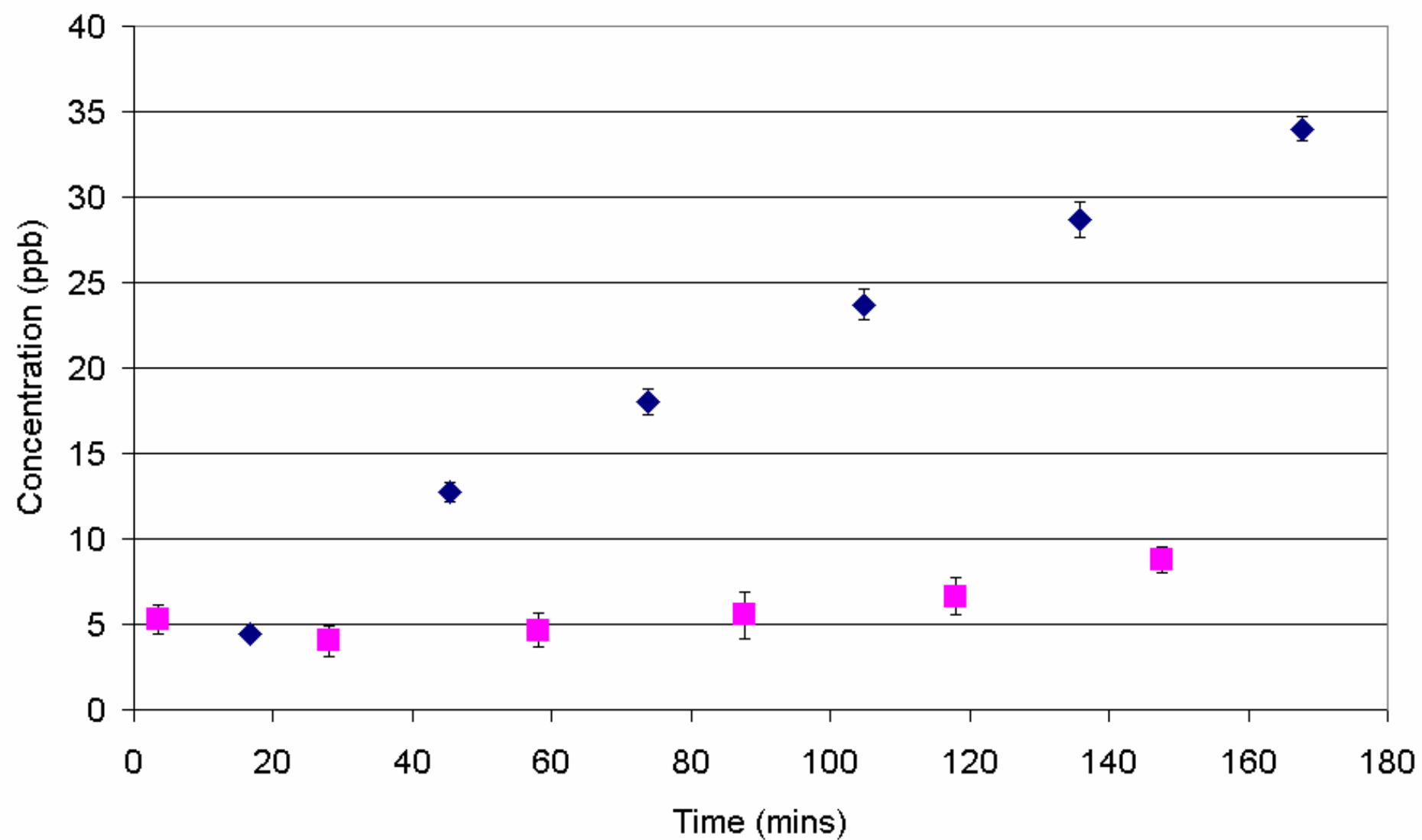


Dr. Wenli Yang, Doniche Derrick; also Rebecca Flock helped build.
Has trailer hitch, and 1000L bag, lamps, fans, all in one unit.

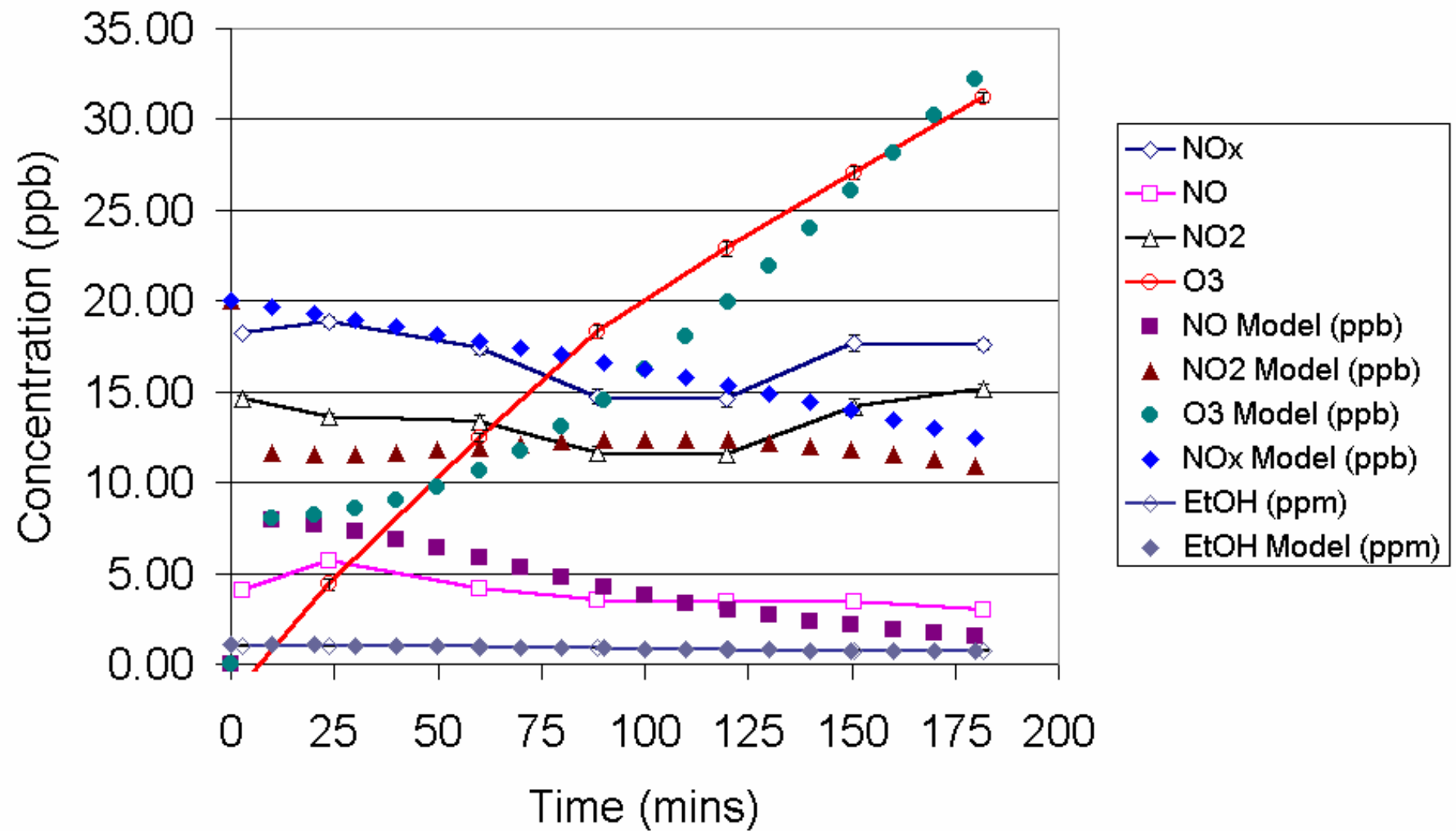
MOChA2 on the road



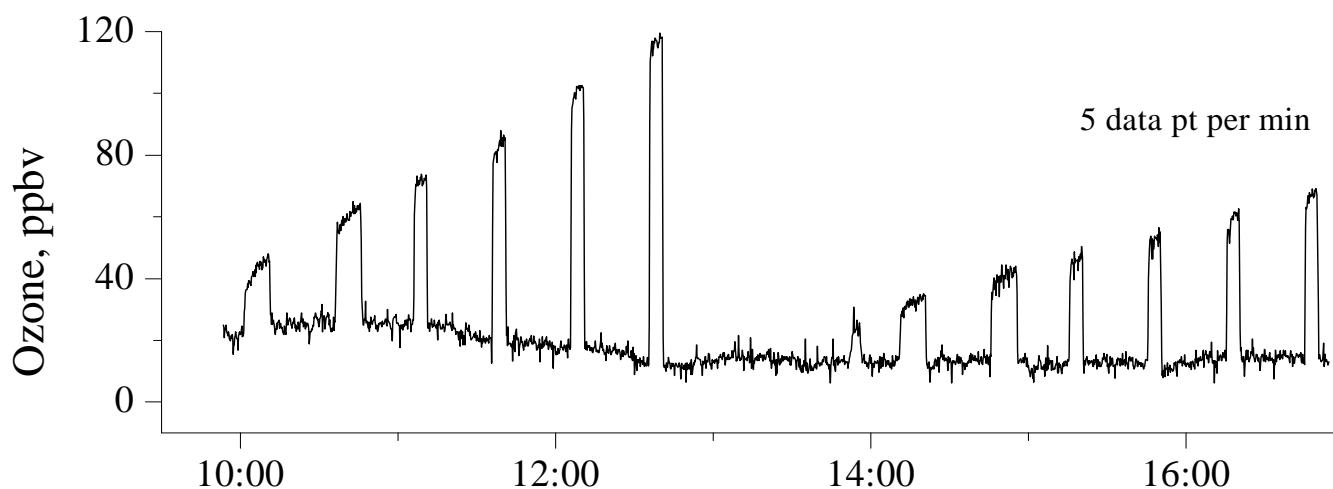
Repeatability and Zero Level Ozone Concentrations



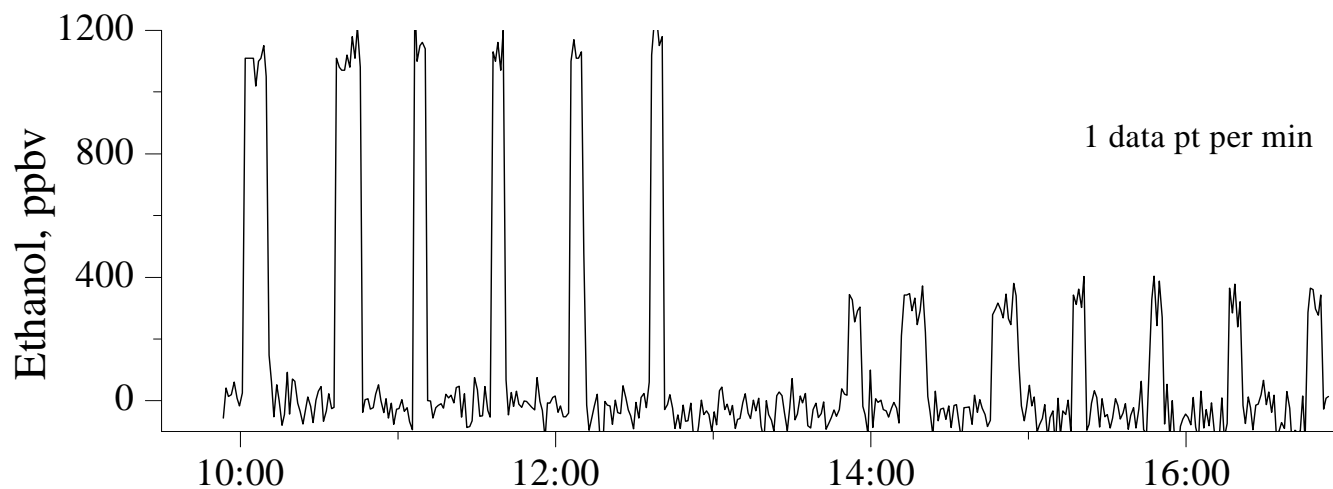
MOChA Measurements (averaged) vs Model Calculations



A dairy example of relative reactivity:
ozone forms, but *not* from the leading VOC!

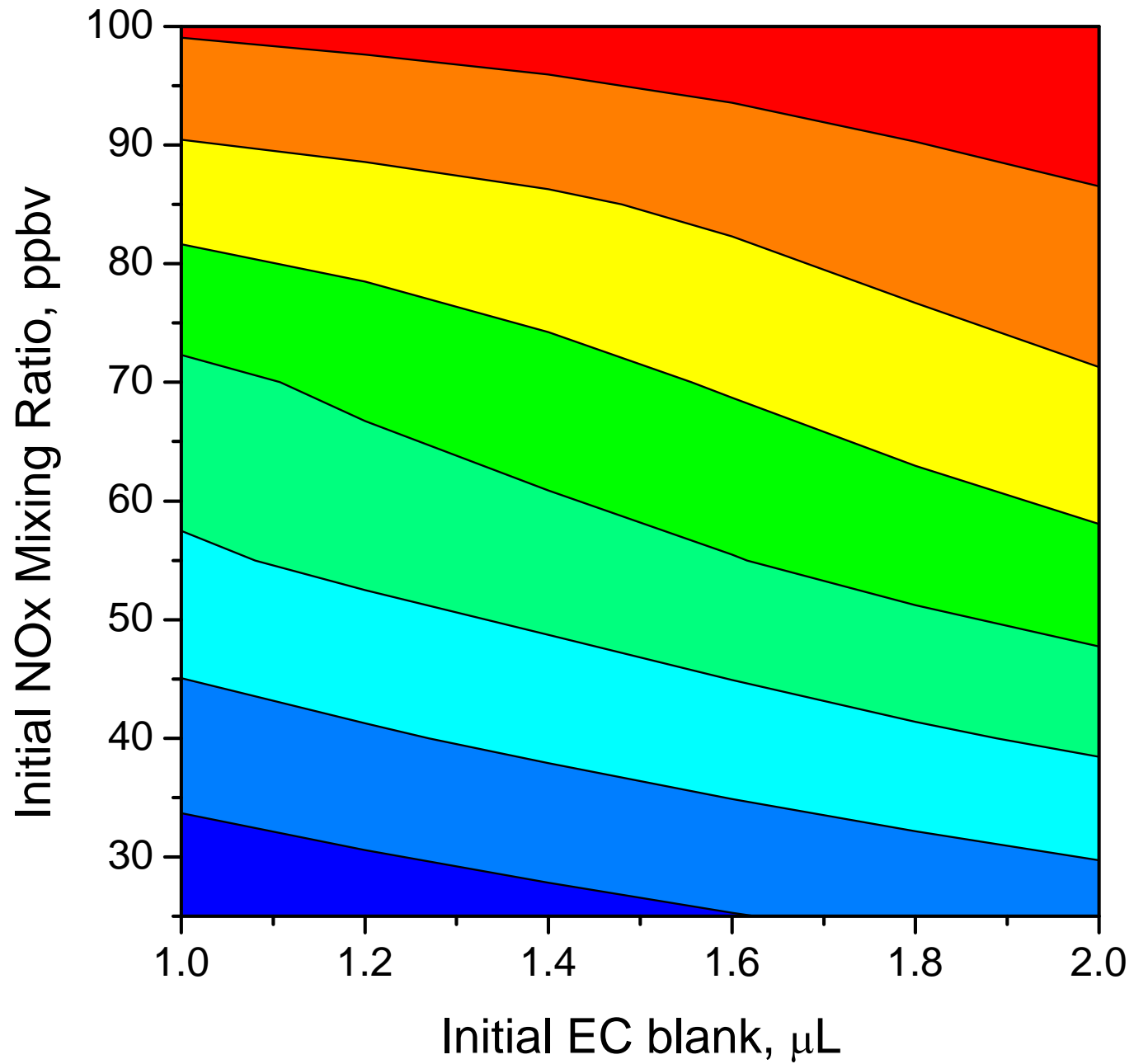


Now, we are following up to identify what these more reactive compounds might be.



Time of Day

EC Blank-NOx Isopleth



San Joaquin Valley Unified Air Pollution Control District

Year: 2020

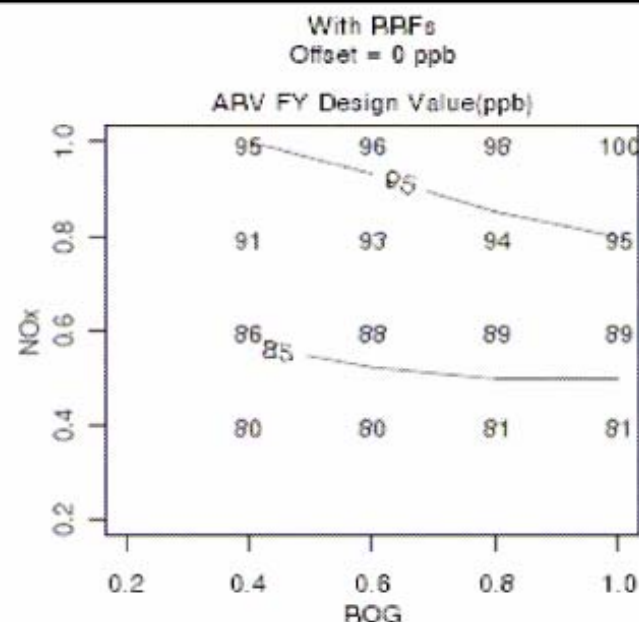
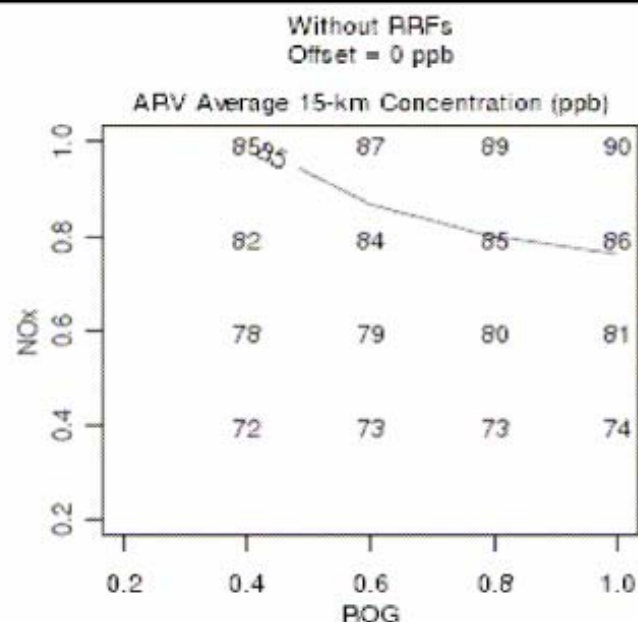
Model: CAMX/MM5/SAPRC99

Site: ARV - Arvin Stn

Subregion: 8

Baseline Year Design Value: 114 ppb

Episode Days	99190	99191	99192	99193	99194	00211	00212	00213	00214	00215
Performance Status	Fail	Fail	Fail	Fail	Pass	Pass	Pass	Pass	Pass	Fail
Peak Observed 8-hour Ozone	102	109	92	54	70	-99	-99	93	105	98
Peak Simulated 8-hour Ozone	84	90	88	76	81	95	98	105	95	88
Peak Simulated 8-hour Ozone within 15 km	94	94	91	81	86	99	103	106	99	98
Baseline Year 15-km, 8-hour Average Ozone	102									
Future Year 15-km, 8-hour Average Ozone	78	79	78	76	78	87	88	93	87	92
Use in RRF Analysis?	No	No	No	No	No	No	No	Yes	Yes	No



Without RRFs
Offset = 40 ppb

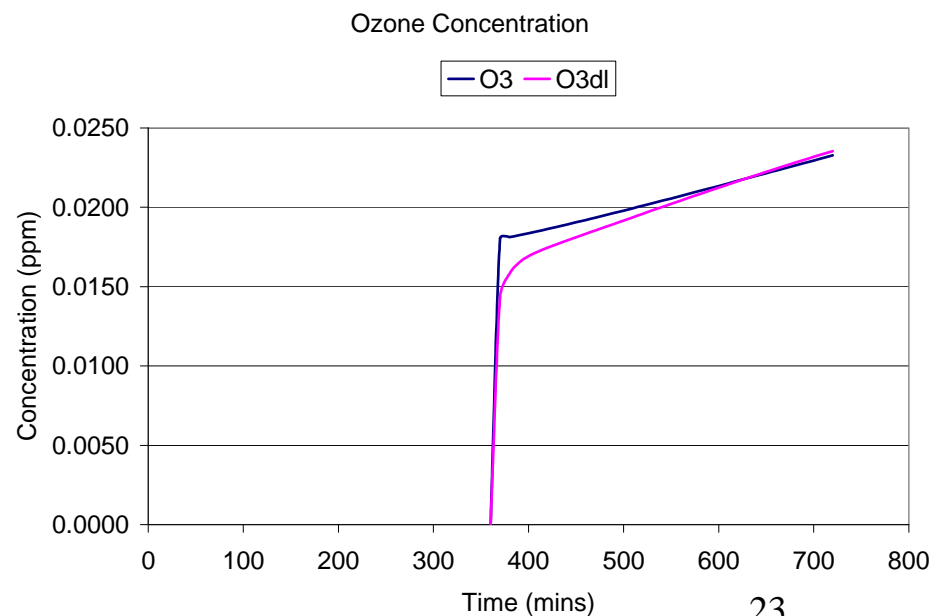
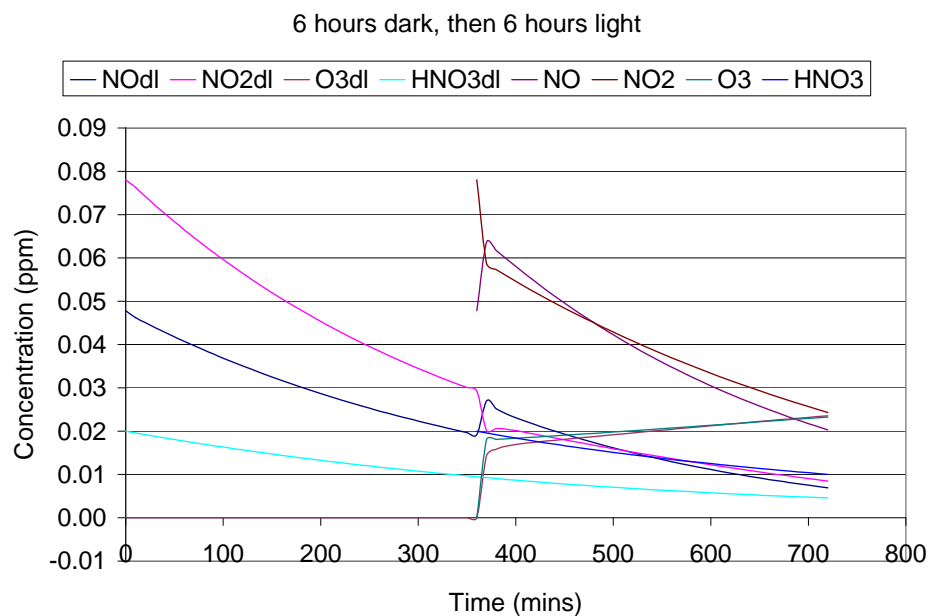
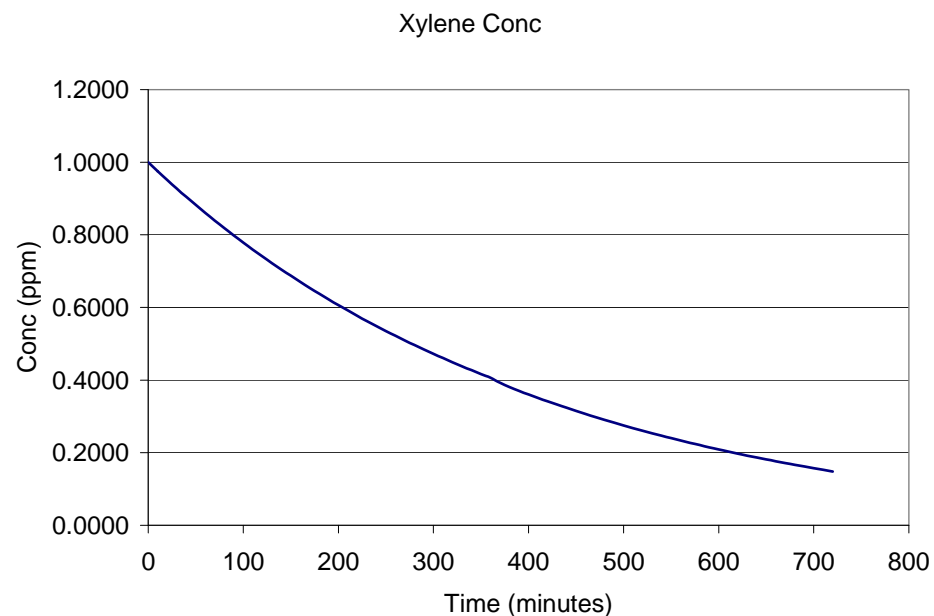
ARV Average 15-km Concentration (ppb)

With RRFs
Offset = 40 ppb

ARV FY Design Value(ppb)

Model calculations for
over-night into next day,
with a highly reactive VOC:

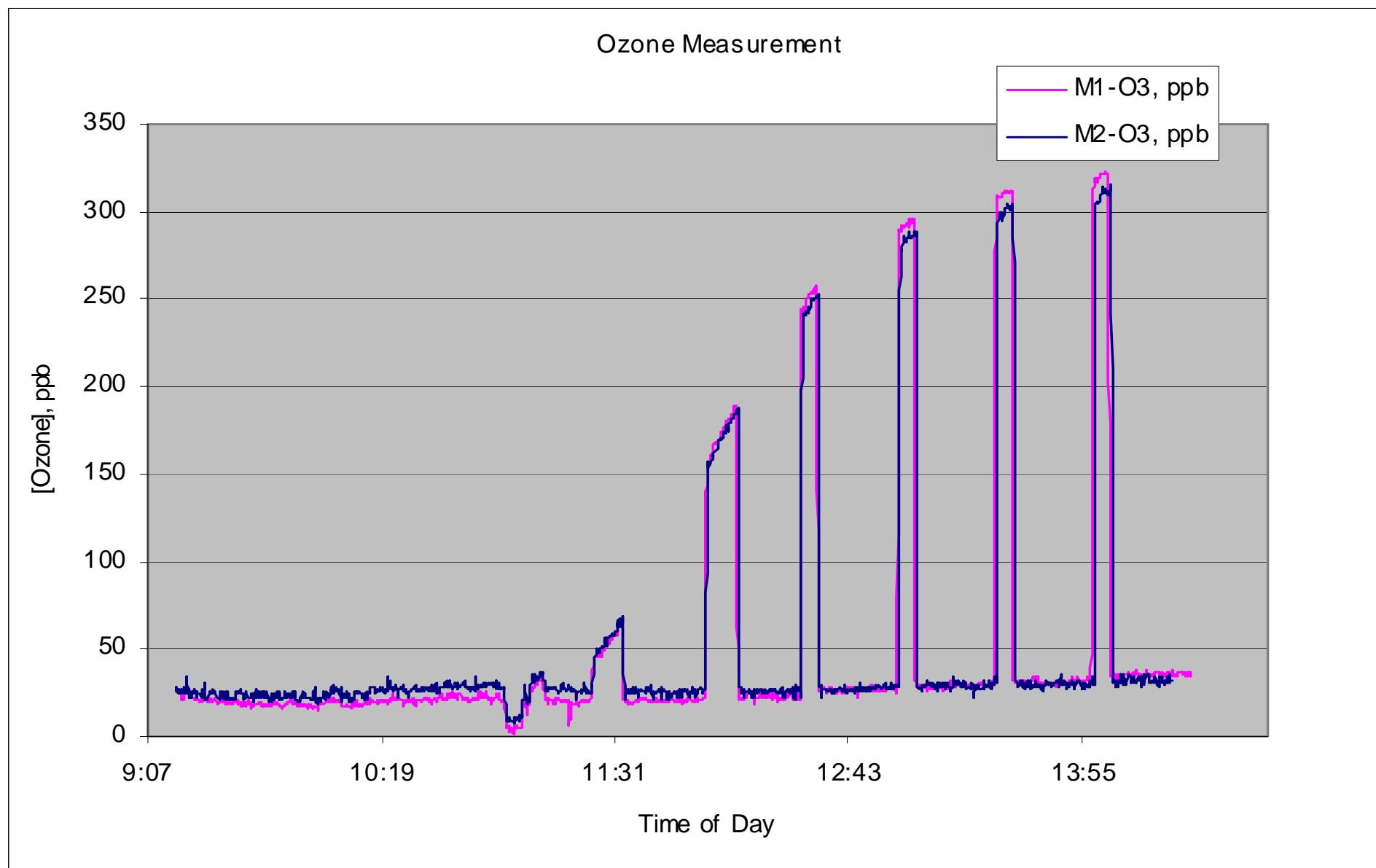
50% reduction in pounds, but
...the same amount of ozone.



Agricultural use is not *all* use!

- Bifenthrin registered use steady
 - about 62,000 lbs in 2004 and 2005
- Bifenthrin sales in 2004 were 109,000 lbs
 - almost double the registered usage!
- Has affected sediment quality
 - But not in agricultural drainages, in suburban streams!

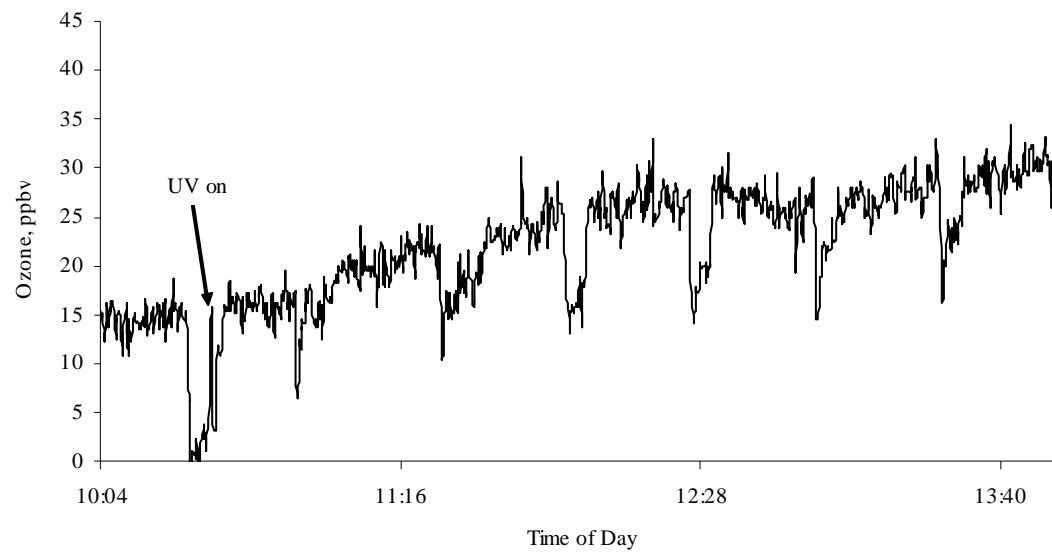
100mL headspace from retail insecticide; ozone in ppb



Retail Dilutable Concentrate Insecticide Spray

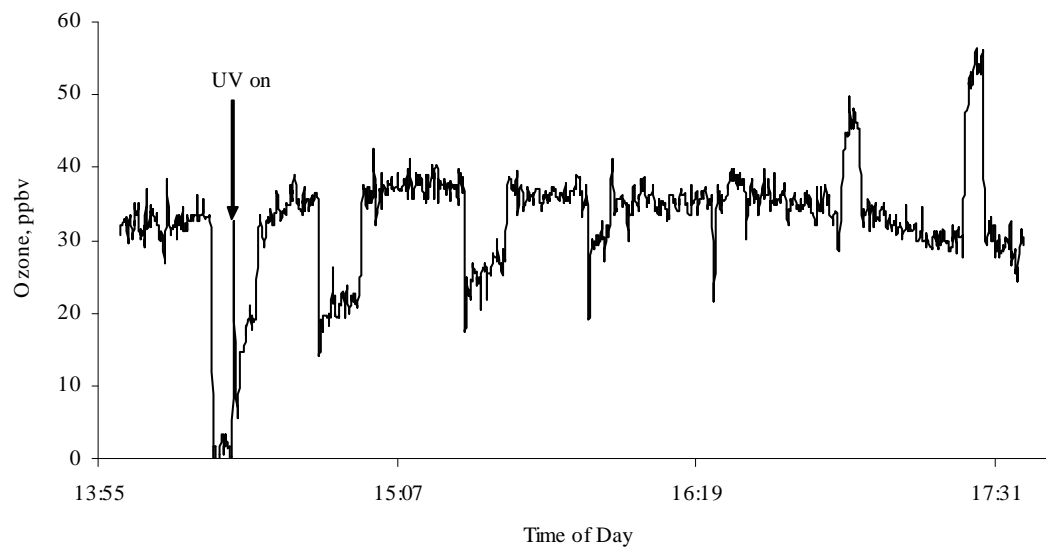
1 mL Headspace from Retail Headspace in 1 m³ Teflon Bag

initial NO_x: 55 ppb



10 mL Headspace from Retail Headspace in 1 m³ Teflon Bag

initial NO_x: 52 ppb



Work in progress

- Evaluating oil-based pesticides
 - Exceedingly low ozone formation!
- Using EC Blank on UCDavis research fields
 - Upwind and downwind
 - Customary dilution into water
 - Assessing contribution from vehicle and soil
- Four field campaigns around Central Valley
 - Various products and formulations
- Computer modelling of low NO_x + mixed VOCs
 - Up to multi-day, regional scale
- To be published in refereed journals
 - Peer-review by other researchers is a vital aspect of quality control and assurance before releasing data

Top 100 pesticides used statewide (all sites combined) in 2005.

Chemical	Rank	Pounds
SULFUR	1	61,229,194
PETROLEUM OIL, UNCLASSIFIED	2	16,108,926
METAM-SODIUM	3	13,035,949
1,3-DICHLOROPROPENE	4	9,319,878
MINERAL OIL	5	9,104,453
METHYL BROMIDE	6	6,444,224
CALCIUM HYDROXIDE	7	4,958,390
CHLOROPICRIN	8	4,864,930
GLYPHOSATE, ISOPROPYLAMINE SALT	9	4,590,893
COPPER HYDROXIDE	10	3,405,369
SULFURYL FLUORIDE	11	3,335,523
COPPER SULFATE (PENTAHYDRATE)	12	3,236,988
PETROLEUM DISTILLATES	13	2,036,895
CHLORPYRIFOS	14	1,993,288

http://www.cdpr.ca.gov/docs/pur/pur05rep/top100_ais.pdf

- **Need to know which organics**
 - Are they high, medium or low reactivity?
 - Otherwise, reducing total pounds could make ozone worse!

Effort reducing the more highly ozone-forming VOCs can get us moving cost-effectively in the right direction. For SJV, a percentage NOx reduction should be several times more effective than generic VOC reduction.

“The number of pounds applied is not as significant as the chemicals that contribute to that total,” said Warmerdam.

“Increased use of less toxic materials shows that we are moving in the right direction.”

(November 14, 2006 press release quoting DPR director; I added underline)

Ambient Air Quality Standards

Pollutant	Averaging Time	California Standards ¹		Federal Standards ²		
		Concentration ³	Method ⁴	Primary ^{3,5}	Secondary ^{3,6}	Method ⁷
Ozone (O ₃)	1 Hour	0.09 ppm (180 µg/m ³)	Ultraviolet Photometry	—	Same as Primary Standard	Ultraviolet Photometry
	8 Hour	0.070 ppm (137 µg/m ³)		0.08 ppm (157 µg/m ³)		
Respirable Particulate Matter (PM ₁₀)	24 Hour	50 µg/m ³	Gravimetric or Beta Attenuation	150 µg/m ³	Same as Primary Standard	Inertial Separation and Gravimetric Analysis
	Annual Arithmetic Mean	20 µg/m ³		—		
Fine Particulate Matter (PM _{2.5})	24 Hour	No Separate State Standard		35 µg/m ³	Same as Primary Standard	Inertial Separation and Gravimetric Analysis
	Annual Arithmetic Mean	12 µg/m ³	Gravimetric or Beta Attenuation	15 µg/m ³		
Carbon Monoxide (CO)	8 Hour	9.0 ppm (10mg/m ³)	Non-Dispersive Infrared Photometry (NDIR)	9 ppm (10 mg/m ³)	None	Non-Dispersive Infrared Photometry (NDIR)
	1 Hour	20 ppm (23 mg/m ³)		35 ppm (40 mg/m ³)		
	8 Hour (Lake Tahoe)	6 ppm (7 mg/m ³)		—		
Nitrogen Dioxide (NO ₂)	Annual Arithmetic Mean	—	Gas Phase Chemiluminescence	0.053 ppm (100 µg/m ³)	Same as Primary Standard	Gas Phase Chemiluminescence
	1 Hour	0.25 ppm (470 µg/m ³)		—		
Sulfur Dioxide (SO ₂)	Annual Arithmetic Mean	—	Ultraviolet Fluorescence	0.030 ppm (80 µg/m ³)	—	Spectrophotometry (Pararosaniline Method)
	24 Hour	0.04 ppm (105 µg/m ³)		0.14 ppm (365 µg/m ³)	—	
	3 Hour	—		—	0.5 ppm (1300 µg/m ³)	—
	1 Hour	0.25 ppm (655 µg/m ³)		—	—	
Lead ⁸	30 Day Average	1.5 µg/m ³	Atomic Absorption	—	—	—
	Calendar Quarter	—		1.5 µg/m ³	Same as Primary Standard	High Volume Sampler and Atomic Absorption
Visibility Reducing Particles	8 Hour	Extinction coefficient of 0.23 per kilometer — visibility of ten miles or more (0.07 — 30 miles or more for Lake Tahoe) due to particles when relative humidity is less than 70 percent. Method: Beta Attenuation and Transmittance through Filter Tape.		No Federal Standards		
Sulfates	24 Hour	25 µg/m ³	Ion Chromatography			
Hydrogen Sulfide	1 Hour	0.03 ppm (42 µg/m ³)	Ultraviolet Fluorescence			
Vinyl Chloride ⁸	24 Hour	0.01 ppm (26 µg/m ³)	Gas Chromatography			

See footnotes on next page ...

For more information please call ARB-PIO at (916) 322-2990

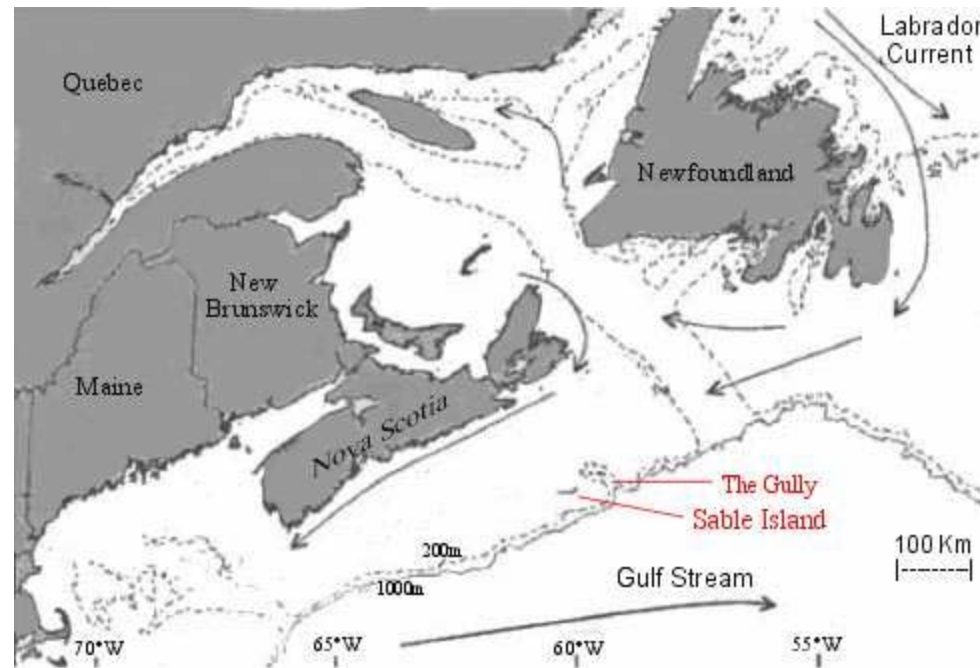
California Air Resources Board (11/10/06)

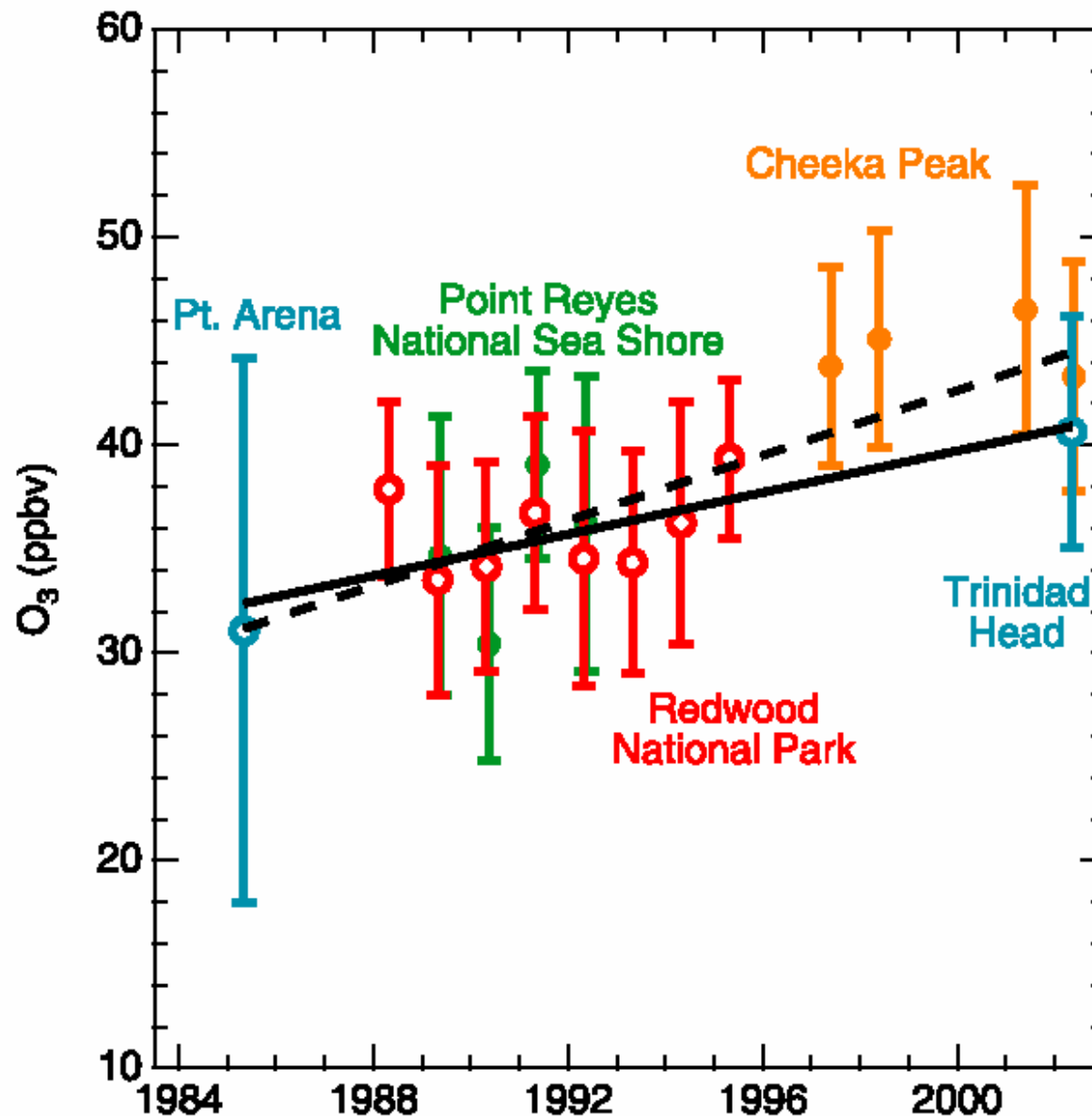
1. California standards for ozone, carbon monoxide (except Lake Tahoe), sulfur dioxide (1 and 24 hour), nitrogen dioxide, suspended particulate matter—PM₁₀, PM_{2.5}, and visibility reducing particles, are values that are not to be exceeded. All others are not to be equaled or exceeded. California ambient air quality standards are listed in the Table of Standards in Section 70200 of Title 17 of the California Code of Regulations.
2. National standards (other than ozone, particulate matter, and those based on annual averages or annual arithmetic mean) are not to be exceeded more than once a year. The ozone standard is attained when the fourth highest eight hour concentration in a year, averaged over three years, is equal to or less than the standard. For PM₁₀, the 24 hour standard is attained when the expected number of days per calendar year with a 24-hour average concentration above 150 µg/m³ is equal to or less than one. For PM_{2.5}, the 24 hour standard is attained when 98 percent of the daily concentrations, averaged over three years, are equal to or less than the standard. Contact U.S. EPA for further clarification and current federal policies.
3. Concentration expressed first in units in which it was promulgated. Equivalent units given in parentheses are based upon a reference temperature of 25°C and a reference pressure of 760 torr. Most measurements of air quality are to be corrected to a reference temperature of 25°C and a reference pressure of 760 torr; ppm in this table refers to ppm by volume, or micromoles of pollutant per mole of gas.
4. Any equivalent procedure which can be shown to the satisfaction of the ARB to give equivalent results at or near the level of the air quality standard may be used.
5. National Primary Standards: The levels of air quality necessary, with an adequate margin of safety to protect the public health.
6. National Secondary Standards: The levels of air quality necessary to protect the public welfare from any known or anticipated adverse effects of a pollutant.
7. Reference method as described by the EPA. An “equivalent method” of measurement may be used but must have a “consistent relationship to the reference method” and must be approved by the EPA.
8. The ARB has identified lead and vinyl chloride as 'toxic air contaminants' with no threshold level of exposure for adverse health effects determined. These actions allow for the implementation of control measures at levels below the ambient concentrations specified for these pollutants.

Regarding idea #3 (up-wind sources):

- “...20% of the violations of the European Council O₃ standard would not have occurred in the absence of anthropogenic emissions from North America.”

Ref: R Vingarzan,
AtmosEnv 2004,
Vol38, p3431.





“Increasing Background
Ozone During Spring on
the West Coast of North
America”

D.Jaffe, H.Price,
D.Parrish, A.Goldstein
and J.Harris

Figure 2. Spring mean mixing ratio ± 1 standard deviation for background O₃ at 5 MBL sites with linear regression lines. The data have been selected by local wind direction